ACE#169

Greatly Reduced Vehicle PGM Content Using Engineered, Highly Dispersed Precious Metal Catalysts

Yong Wang (PI) (WSU)
Holmes Ahari, **Vencon Easterling, Kiran Premchand** (Stellantis)
Yipeng Sun, Pascaline Tran (BASF)
Konstantin Khivantsev, Shari Li, Janos Szanyi (PNNL)
Abhaya Datye (UNM)

2022 AMR, June 21, 2021

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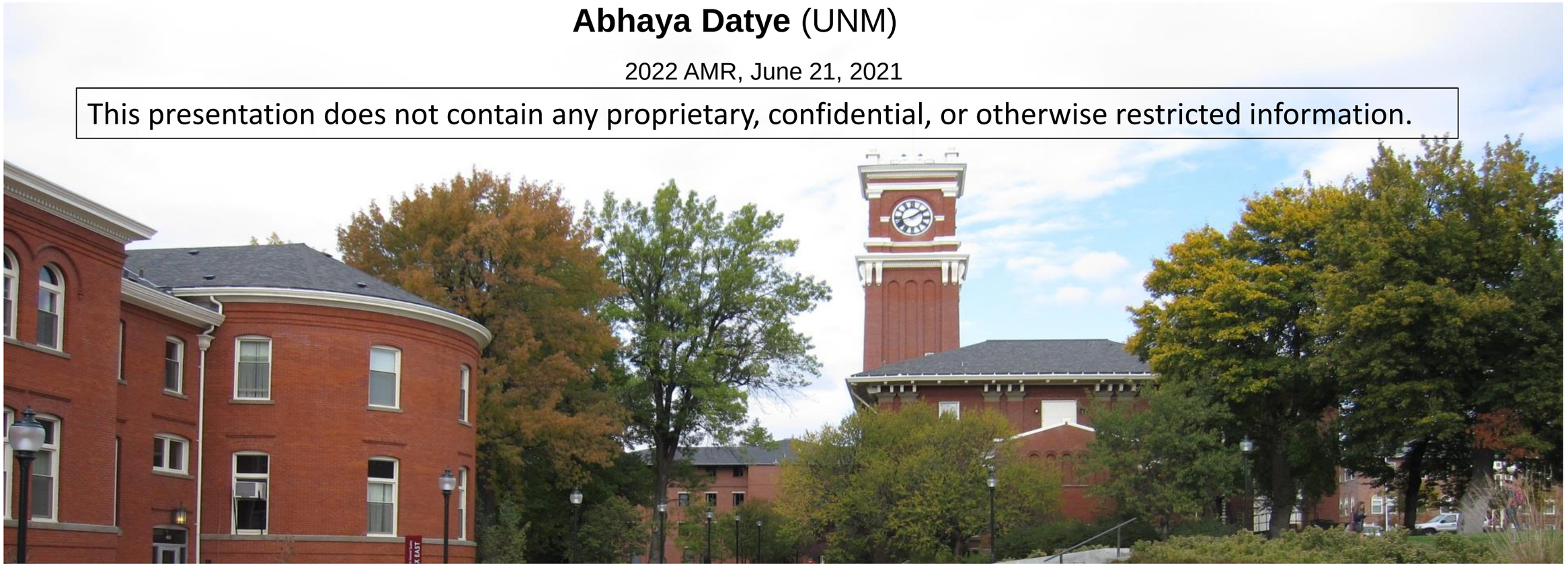


Overview

Timeline

- 39-mon project funded by FOA DE-FOA-0002197
- Status:
  - Start date – Oct. 1, 2020
  - End date – Dec. 31, 2023

Budget

- DOE share: $2.5M
  - WSU: $790K
  - Stellantis : $195K
  - BASF: $195K
  - PNNL: $780K
  - UNM: $540K
- Cost share: $625K
  - Stellantis: $325K
  - BASF: $300K

Barriers

- Lack of cost-effective and sustainable emission control
- Durability of emissions control devices

Partners

- WSU
- Stellantis
- BASF
- PNNL
- UNM

WASHINGTON STATE UNIVERSITY

BASF We create chemistry

Pacific Northwest NATIONAL LABORATORY

Relevance

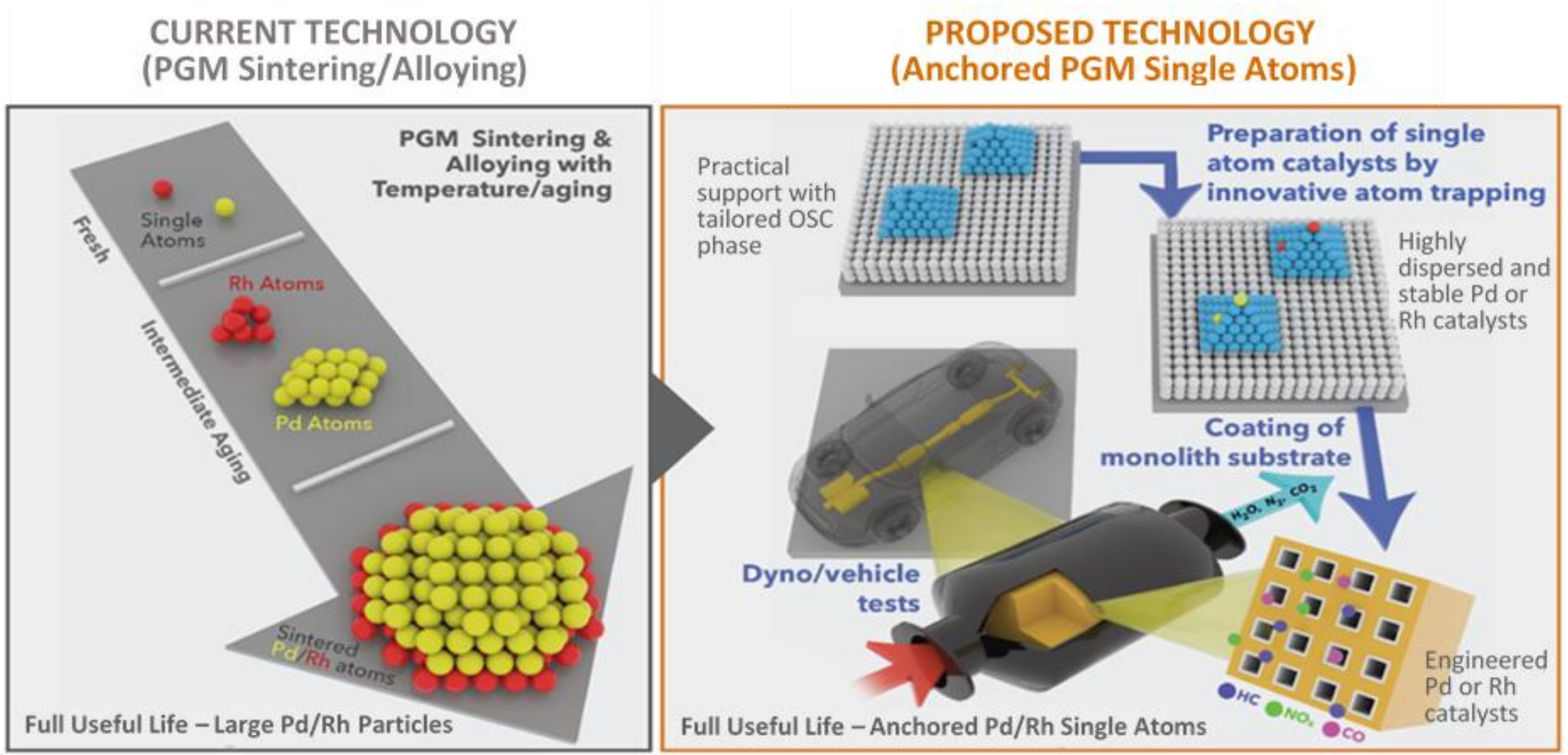
- Minimize PGM content in stoichiometric three-way catalyst systems for greater strategic material sustainability and cost competitiveness
- Provide high reactivity at low temperatures (USCAR 150˚C Challenge) to remediate cold start emissions
- Assure Bin30/SULEV30 emissions compliance, which requires near 100% conversion efficiency over the full useful life of the vehicle
  - Mitigate sintering, intermixing, and alloying of the PGM components
  - Minimize the detrimental effect of poisons derived from the fuel and lubricants

Our end goal is to demonstrate vehicle FTP, US06, and HWFE test performance on par with current (SULEV30/20) systems that employ 2x-4x higher levels of PGM.

Milestones

Month/Year	Description of Milestone or Go/No-Go decision	Status
3/2021	Demonstrate the atom trapping method using commercial supports	√
6/2021	Identify commercial baseline supports for further development	√
9/2021	Replicate the synthesis of atom trapping with commercial supports at >10 gram scale	√
12/2021	***Go/No-Go***: Scalable synthesized powder catalysts exhibit similar or better performance than baseline powder catalysts with a factor of 2x-4x reduction in PGM content	√
3/2022	Synthesize 100 grams catalysts using atom trapping for core sample preparation	√
6/2022	BASF provides cores for testing	On track
9/2022	Replicate the powder catalyst synthesis by atom trapping at 500 gram scale	On track
12/2022	***Go/No-Go:*** Core samples must meet or exceed the baseline catalysts with a factor of 2x-4x reduction in PGM content	On track

Approach



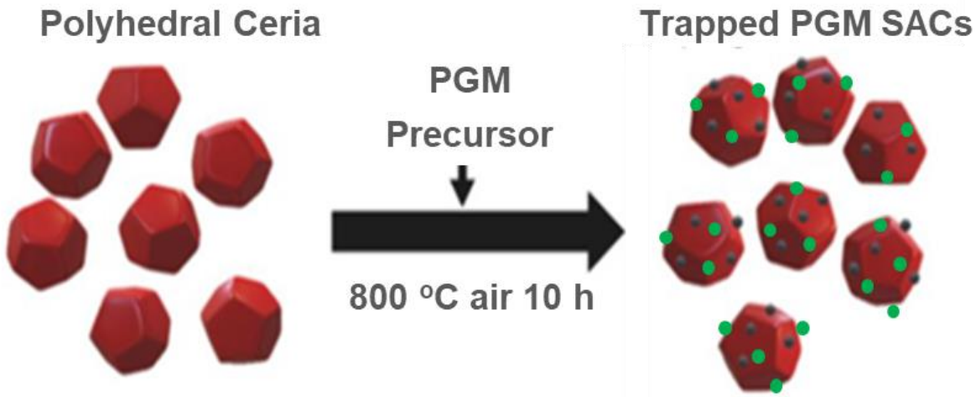
C.K.Lambert, ***Nature Catalysis*** 2019, 2, 554–557
S.B.Kang, S.H.Oh, et al, ***Chem.Eng.J.*** 2017, 316, 631-644

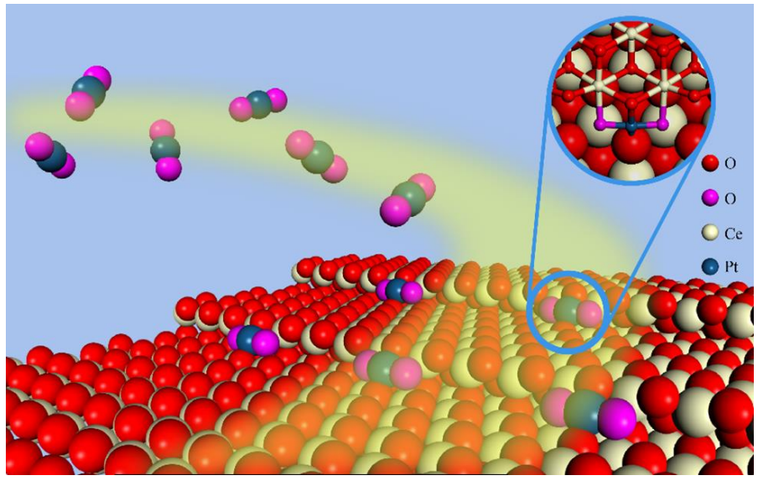
Jones *et al*, ***Science,*** 2016, 353 (6295),150-154; Kunwar *et al*, ***ACS Catalysis***, 2019, 9, 3978-3990; Alcala *et al*, ***Appl.Catal.B***, 2021, 10.1016/j.apcatb.2020.119722

Overcome major limitations of current TWCs (sintering/alloying) by employing atom trapping (*at*SACs) technology to create highly dispersed and stable catalysts.

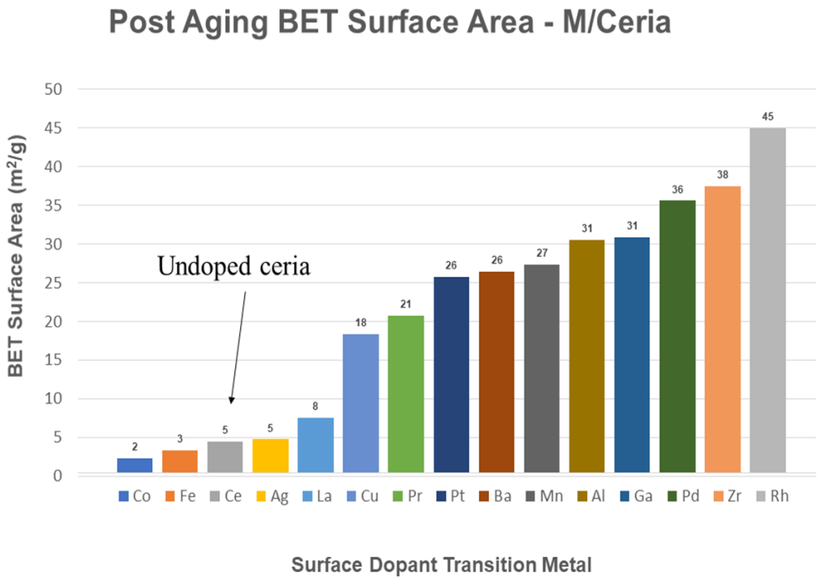
Approach

Preparation of thermally stable SACs on ceria by atom trapping

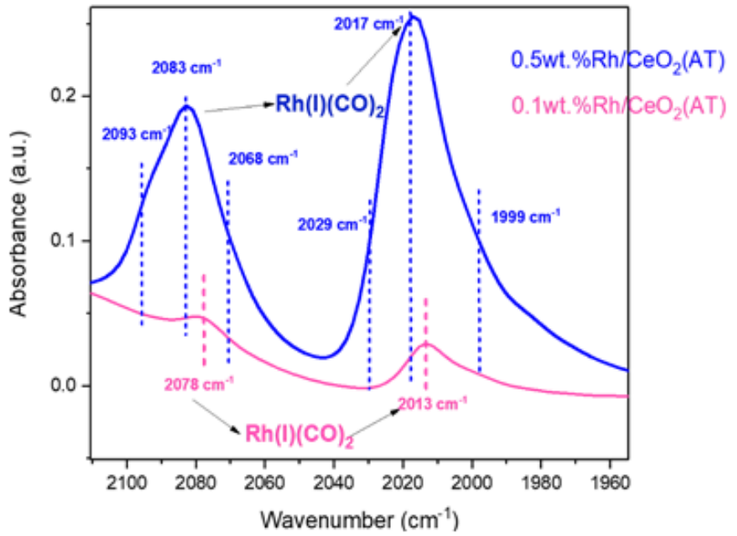


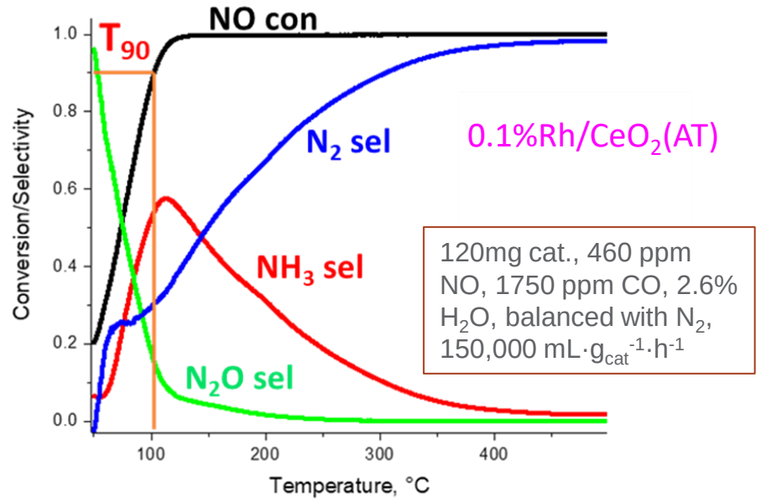


Kunwar *et al.*, ***ACS Catalysis***, 2019, 9, 3978-3990



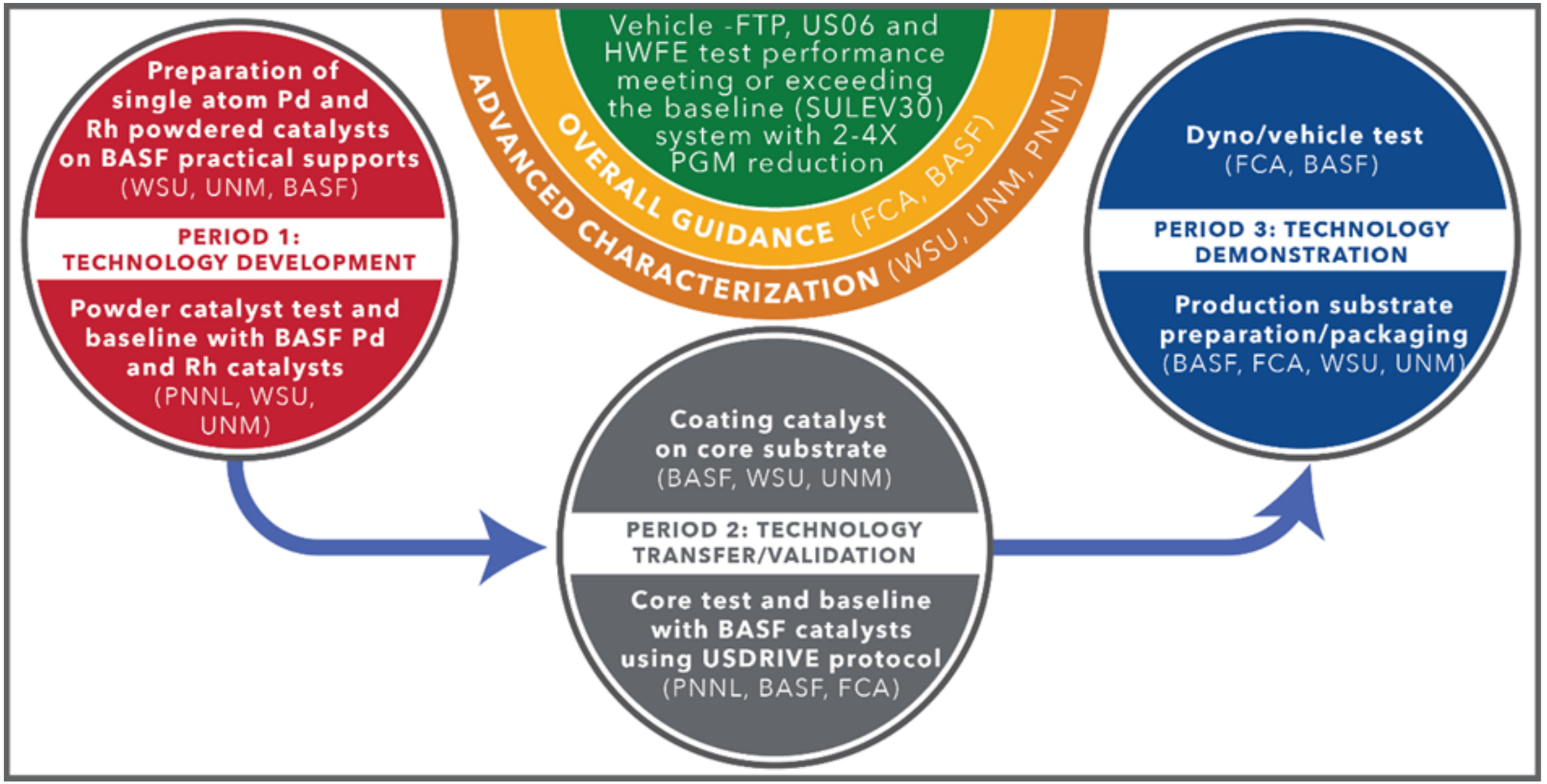
Alcala *et al*, ***Appl.Catal.B: Envi.***, 2021, 284, 119722





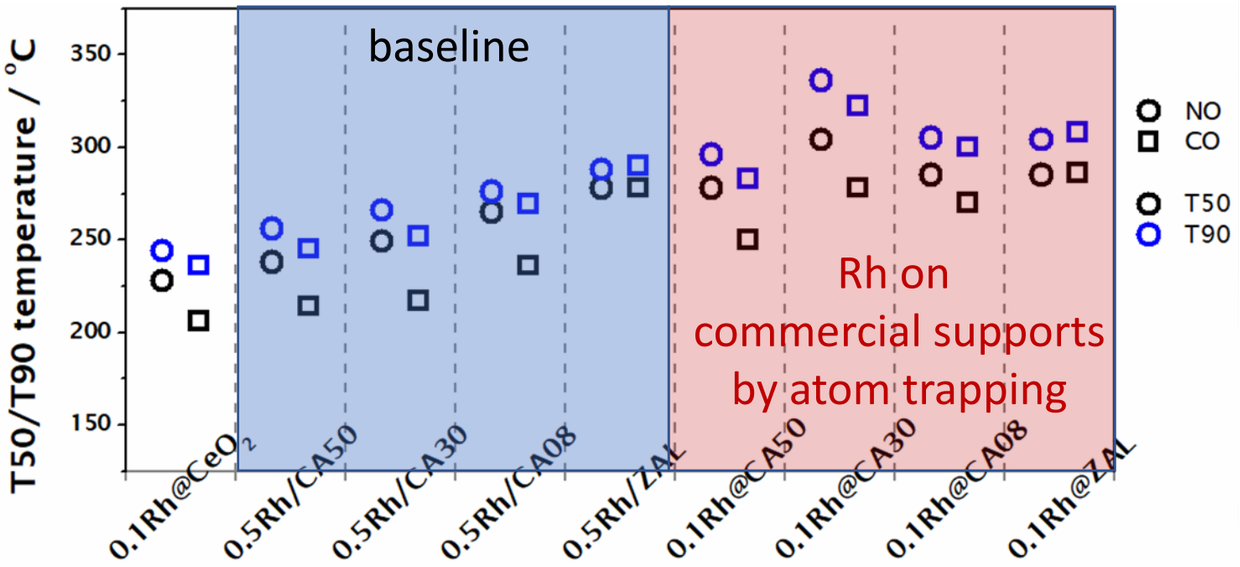
Khivantsev *et al*, ***Angew.Chem.Int.Ed***., 2021, 60(1), 391-398

Scope and Overall Objective



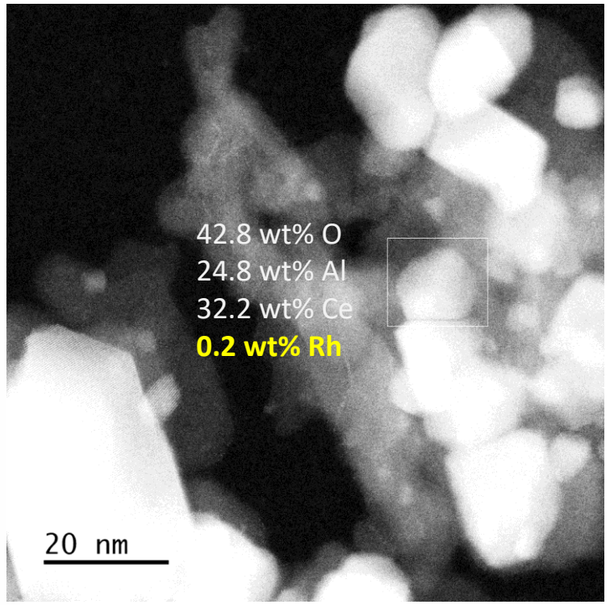
Technical Accomplishments and Progress

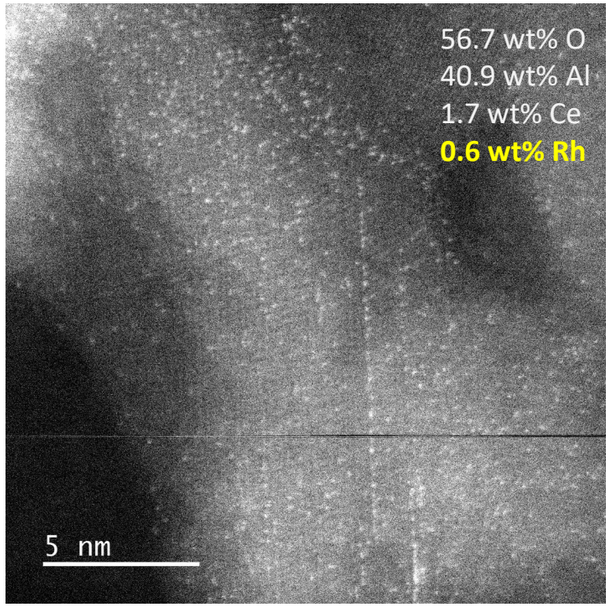
Atom trapping of Rh on commercial supports

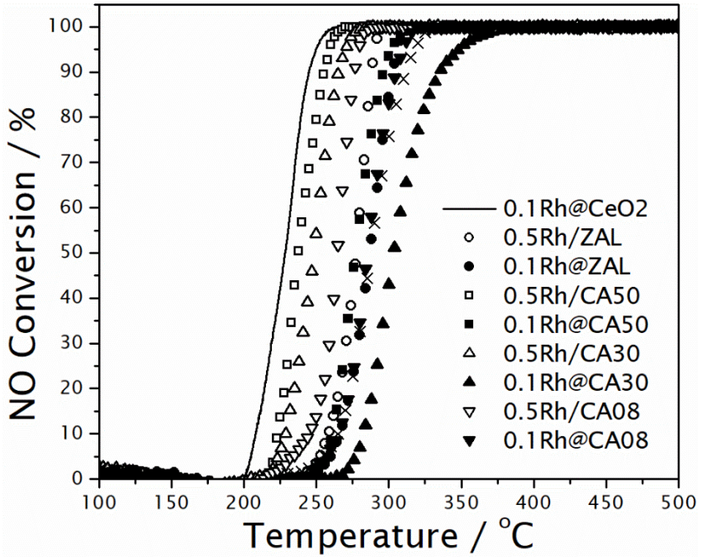


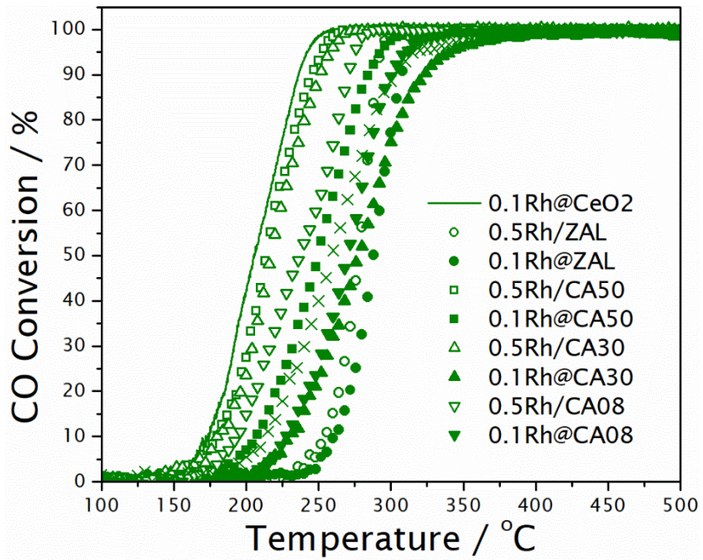
2nd LOCs after HTA (800 °C, 10h, 10 % H_2O), 450 ppm NO, 2350 ppm CO, 950 ppm O_2, 4.5 % H_2O, N_2 balance, WHSV = 150 L/g-h, λ = 1

Rh is detected on ceria and alumina (AC-STEM of 0.1Rh@CA50)





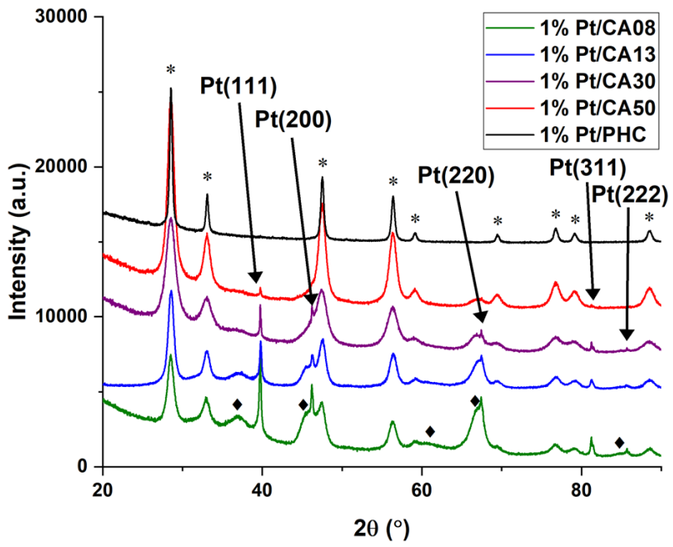


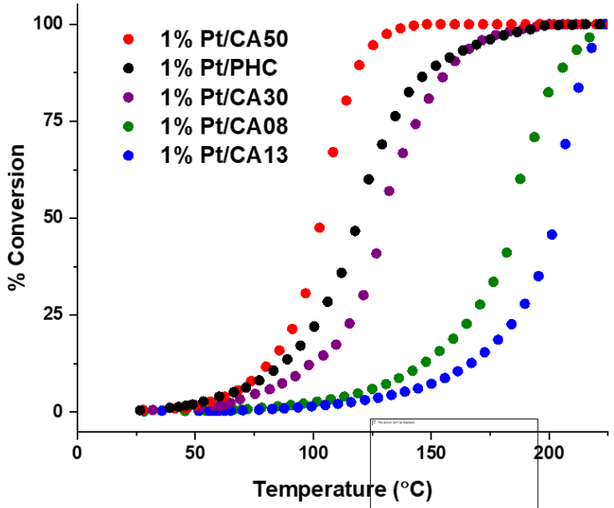


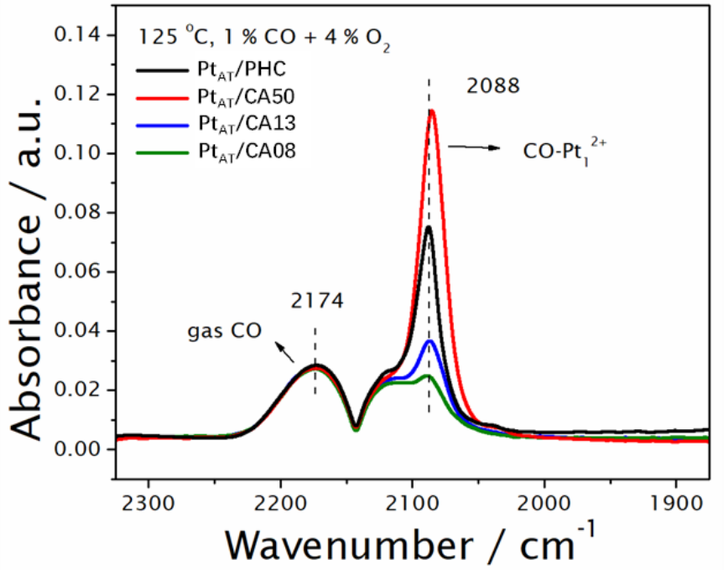
- Similar performance of 0.1wt%Rh on ceria by atom trapping as baselines with 0.5wt% Rh
- Poorer performance of 0.1wt%Rh on commercial supports by atom trapping than that on ceria – Rh is detected on both ceria and alumina by AC-STEM
- Identified the areas for further improvement

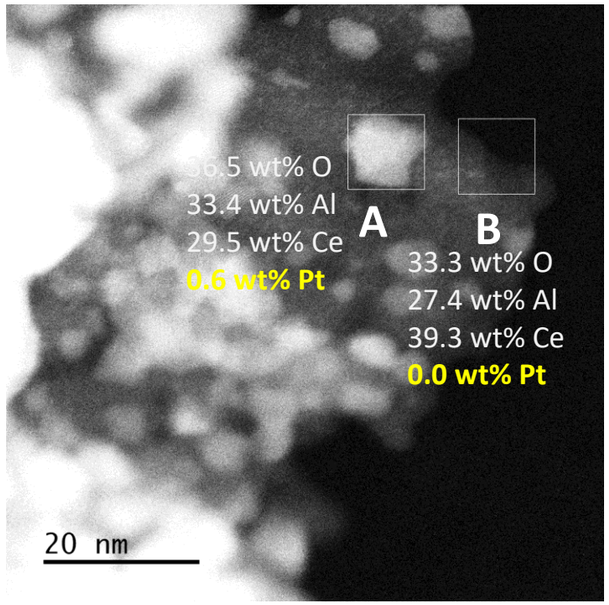
Technical Accomplishments and Progress

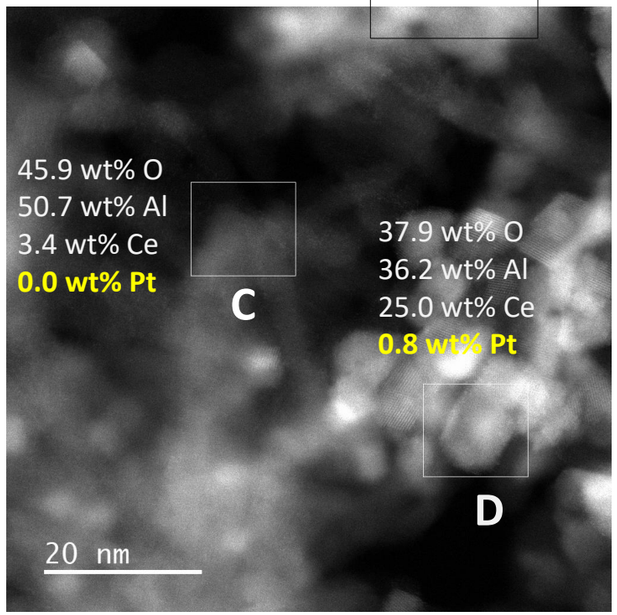
Ceria crystallites are much more efficient in atom trapping than isolated Ce cations on alumina









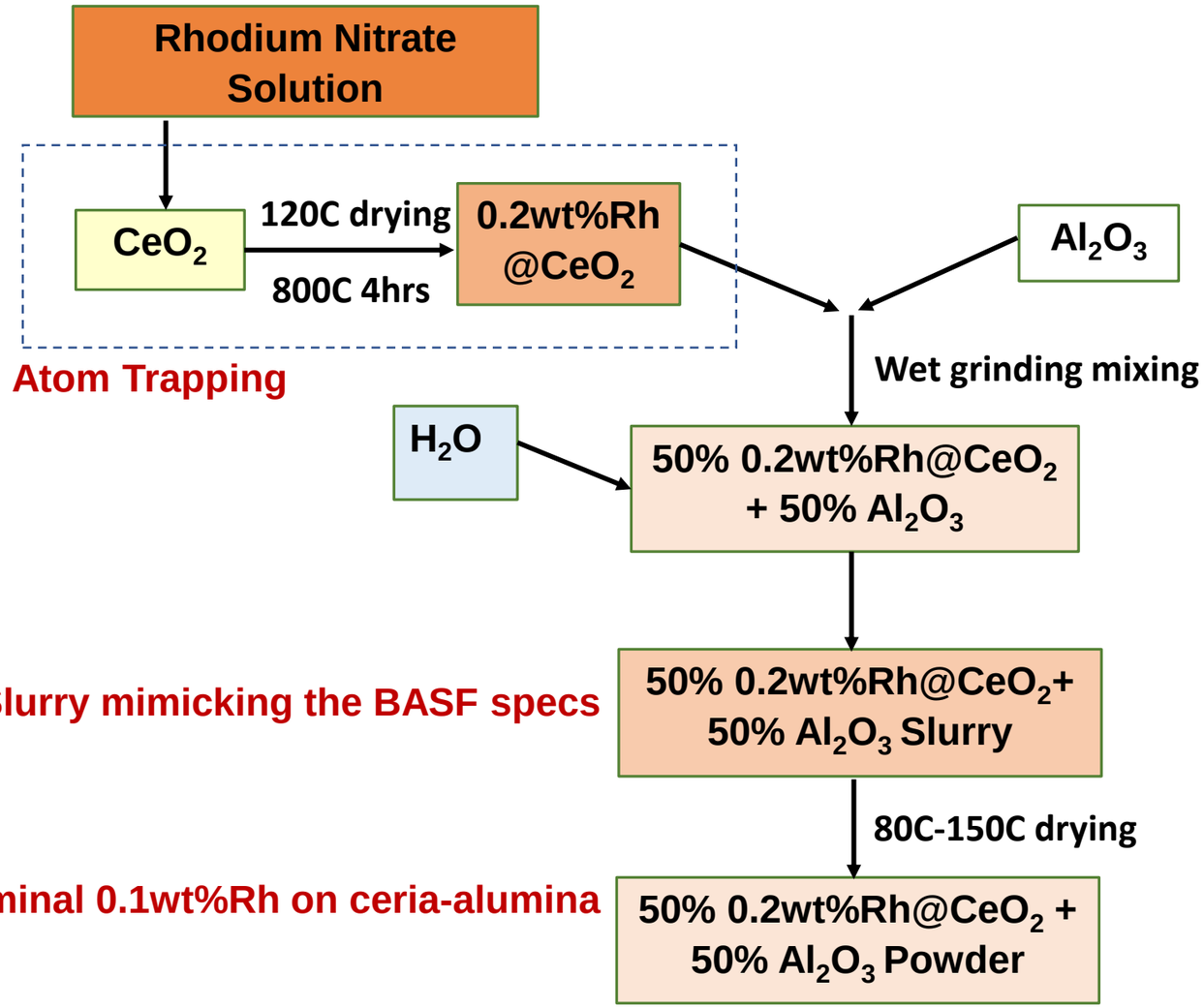


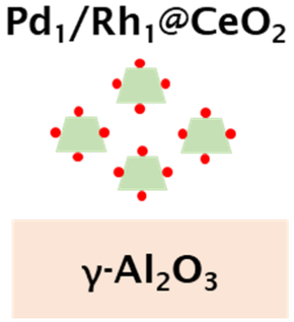
Pt was used to probe the atom trapping efficiency of commercial supports containing alumina:

- Dispersion of Pt is dependent on the ceria content
- Ceria crystallites trap Pt atoms (regions A and D) while isolated Ce cations on alumina do not (regions B and C).
- The trapping of isolated Pt atoms is less efficient as ceria loading decreases.

Pham *et al.*, ***ACS Sus.Chem.Eng.***(revisions submitted)

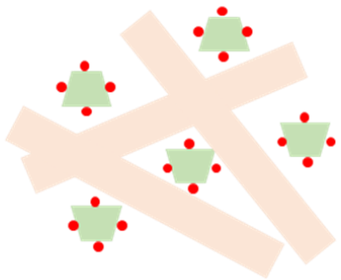
Technical Accomplishments and Progress
New strategy was developed to selectively deposit Rh on ceria on BASF supports

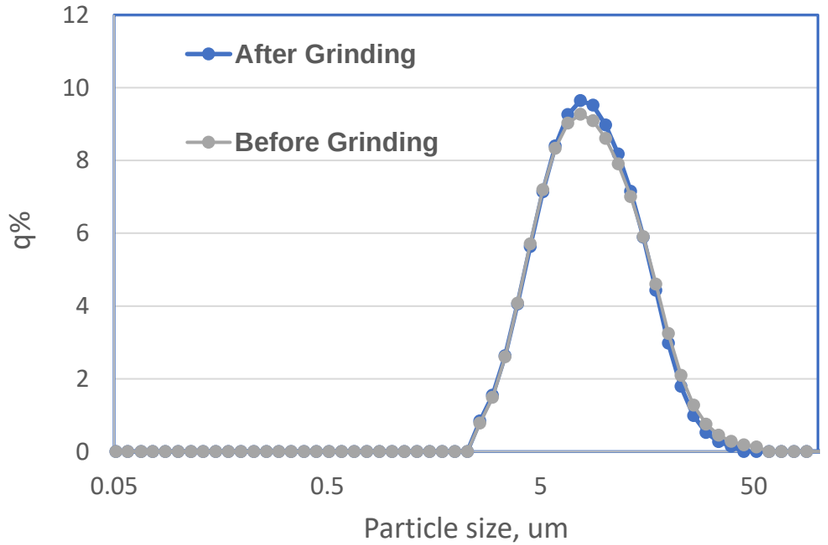




Wet, mimicking the slurry characteristics by BASF

ball milling for mixing





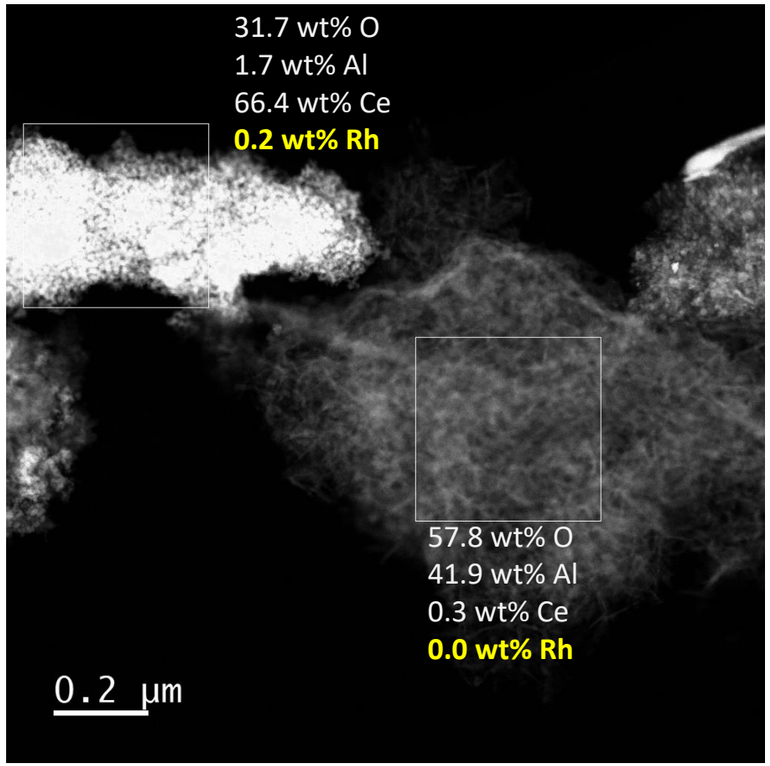
D50: ~8 um, D90: ~17 um

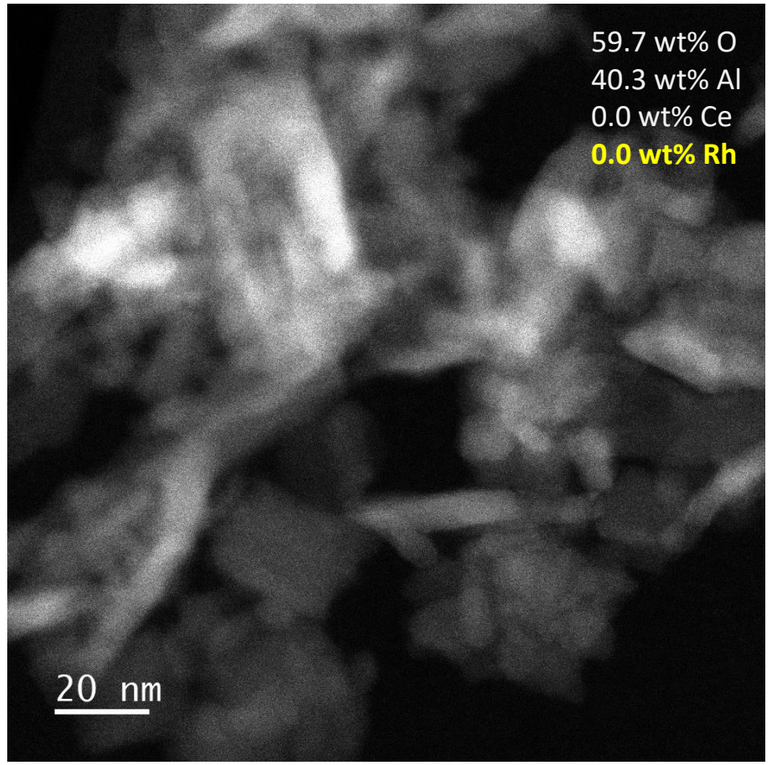
BASF suggested : D50: 3-6 um and D90: 10-16 um

- BASF ceria and alumina supports were used
- Target similar particle size, rheological properties etc in BASF scaled-up slurry preparation

Technical Accomplishments and Progress

AC-STEM images of 0.1Rh@ceria-alumina: Rh is selectively deposited on ceria



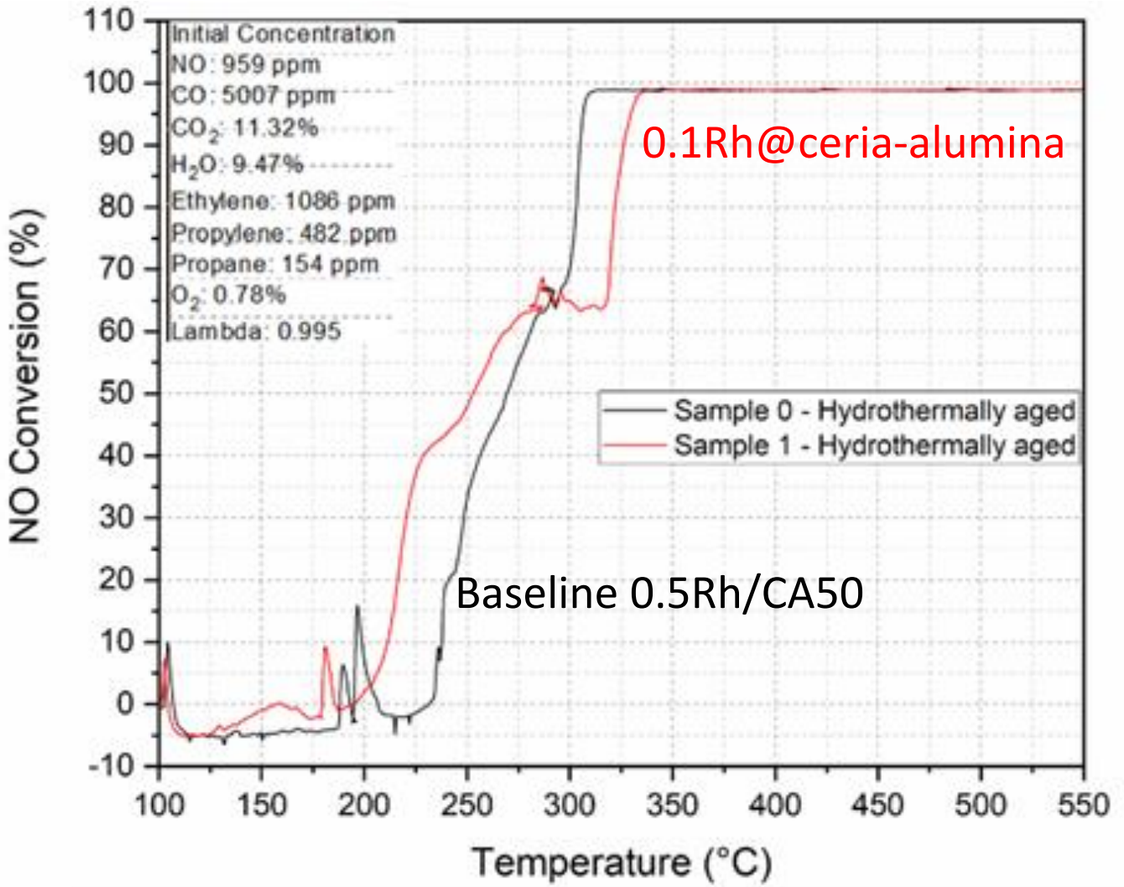


- AC-STEM coupled with EDS characterization confirms that no Rh is detected on the alumina, and instead, Rh is retained on ceria and is not transferred to the alumina.

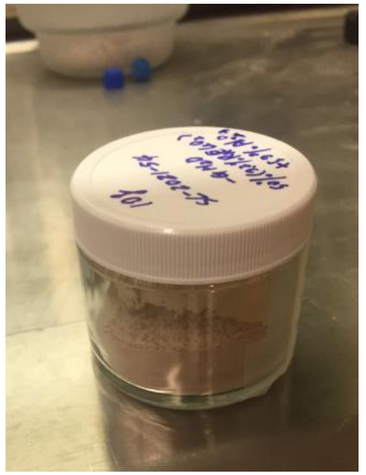
JEOL NEOARM 200CF microscope located in a room with ¼ thick seam welded Al on all 6 sides, a radiant cooling system - with very low air flow to avoid convection currents and excellent sound isolation.

Technical Accomplishments and Progress

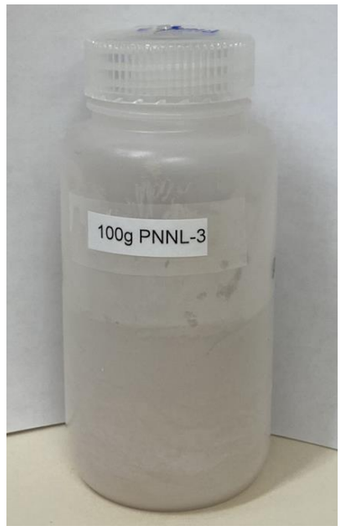
Similar performance on baseline 0.5Rh/CA50 (sample 0) and 0.1Rh@ceria-alumina (sample 1, by atom trapping), both hydrothermally aged (950 ºC, 5 hours)



Pretreatment at 600 ºC for 20 min under reaction concentrations.
Light-off from 100 ºC to 550 ºC at a rate of 5 ºC/min



>10 g



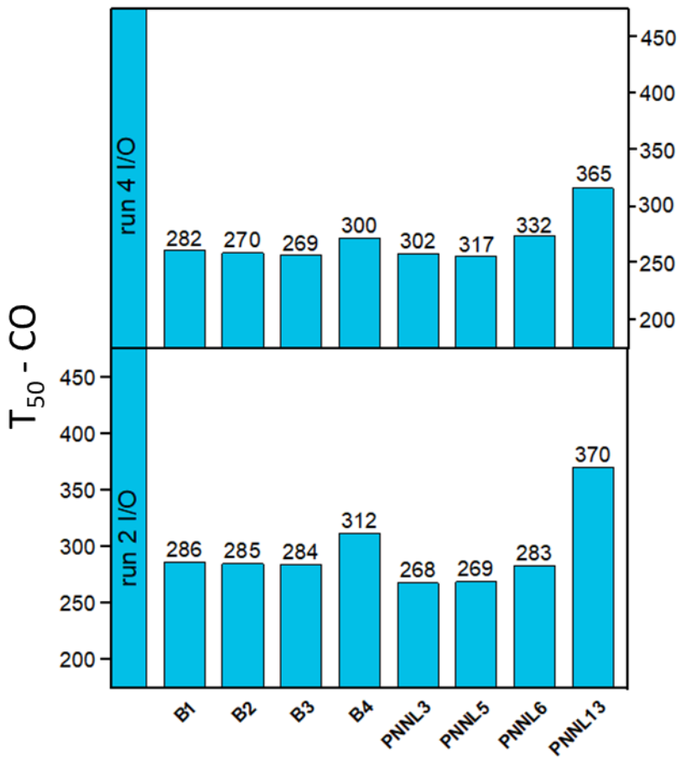
100 g

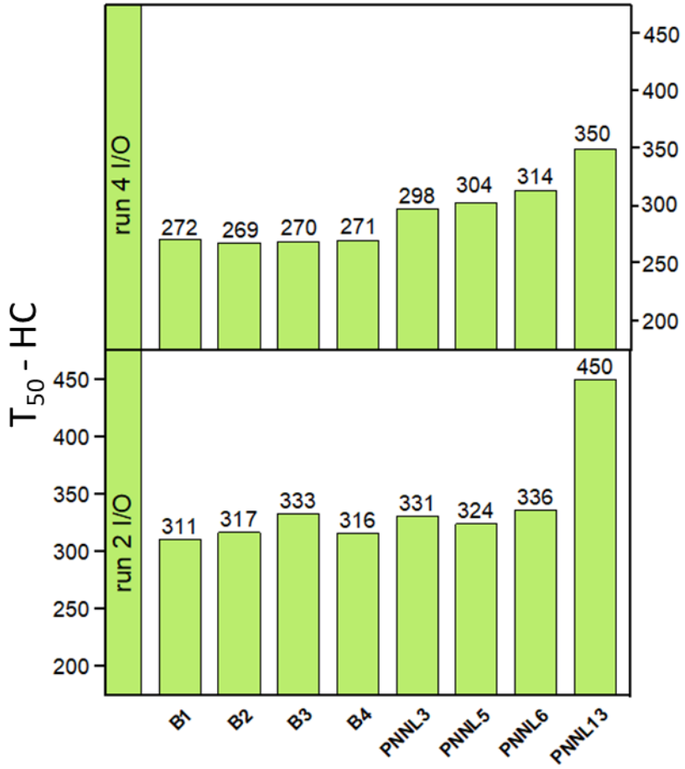
Wet grinding mixing

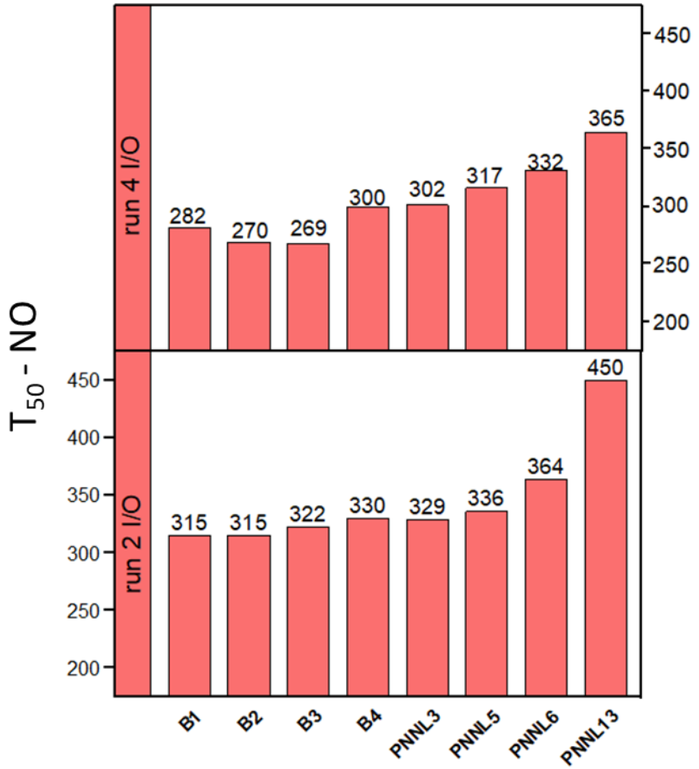
- US DRIVE Protocols were used to compare the baseline catalyst and the catalyst prepared by atom trapping
- Scaled up the synthesis required for core substrate washcoating.

Technical Accomplishments and Progress

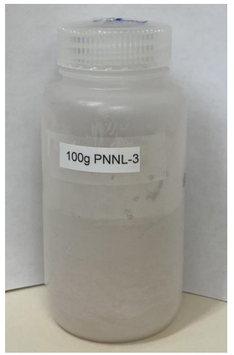
Comparison of T_{50} for CO, HC, and NO conversion performed by BASF







PNNL3



100 g

HTA: 980°C for 5hrs, 10% steam (3min lean/3 min rich)

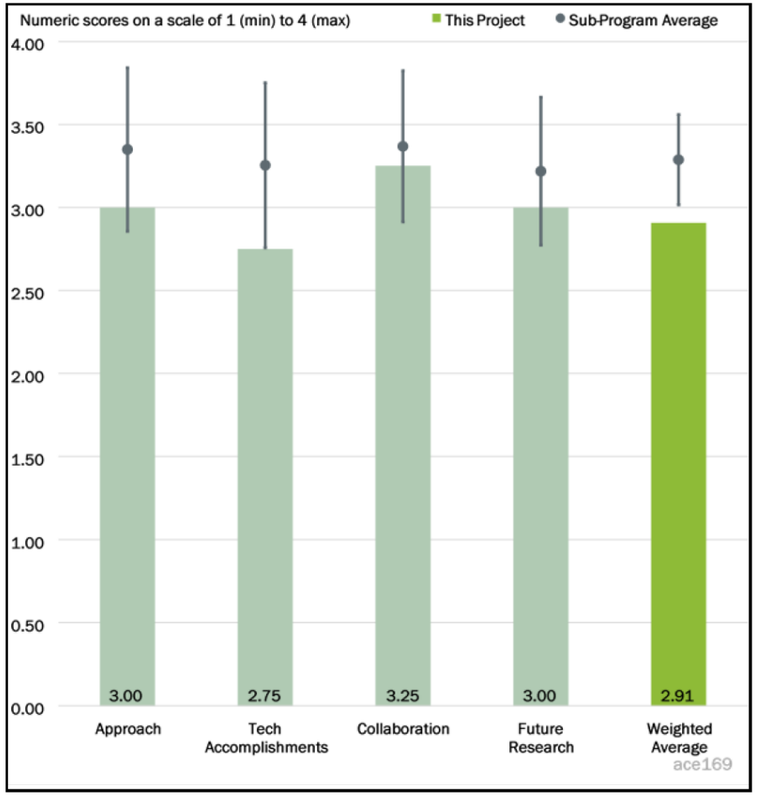
Testing conditions: GHSV = 70,000 hr^{-1}, oscillating feed (1s lean – 1s rich), feed contains CO, H_2, O2, HC (C3, $C3^=$), NO, CO2, H2O

- 1st light-off at λ = 1.00, cool down in lean (λ = 1.05)
- 2nd light-off at λ = 1.00 – **run 2 l/O**
- λ-sweep from lean to rich (1.05, 102, 101, 1.00, 0.99, 098, 096) at 450 and 350C, cool down in lean (λ = 1.05)
- 4th light-off at λ = 1.00 – **run 4 2 l/O**

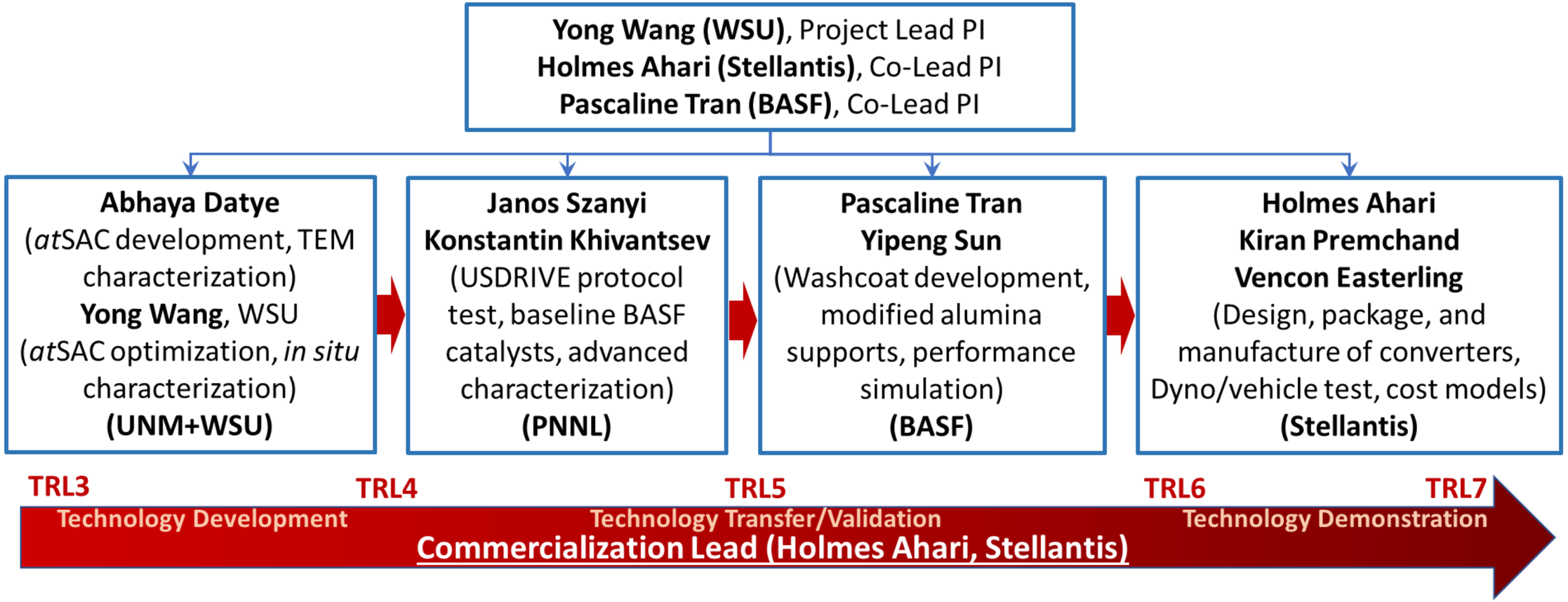
- Improved performance of catalysts prepared using atom trapping (PNNL2>PNNL5>PNNL6>PNNL13) by optimization of
  - Selective deposition of Rh on ceria domains
  - Atom trapping steps
  - Support content
- PNNL3 exhibited similar performance as baseline catalysts (B1-B4), but with 5x less Rh, and was chosen for core substrate washcoating

Responses to Previous Year Reviewers' Comments

Reviewers' Comments	Responses
Identify any barriers for commercialization as early as possible	A major focus of Budget Period 1 scope
The baseline catalyst will need to be retested with the U.S. DRIVE protocol conditions in order to validate future results of new catalysts.	Baseline and catalysts prepared by atom trapping were compared not only with the U.S.DRIVE protocol but also at BASF.
It will be good to see the approach proposed scaled up to larger sizes for washcoating.	Scaling up the synthesis to larger sizes is one of the major go/no-go decision for Budget Period 1.



Collaboration and Coordination with Other Institutions



Acknowledgements

DOE Vehicle Technologies Program:

Siddiq Khan, Gurpreet Singh

WASHINGTON STATE UNIVERSITY

Remaining Challenges and Barriers

- Performance of powder catalysts prepared by atom trapping can be translated to core samples
- Understand possible catalyst deactivation, e.g., by phosphorous, and develop regeneration strategies
- *at*SACs can be scaled up required for production substrate washcoating
- Demonstrate cost saving advantages at TWC system and vehicle-level

Proposed Future Research

- Slurry preparation/characterization for washcoating substrate
- Core sample preparation and characterization
- Demonstration of target catalytic performance with washcoated cores
- Evaluation of the effect of phosphorous on catalyst performance
- Scale up synthesis of *at*SAC powder catalysts to >500 grams

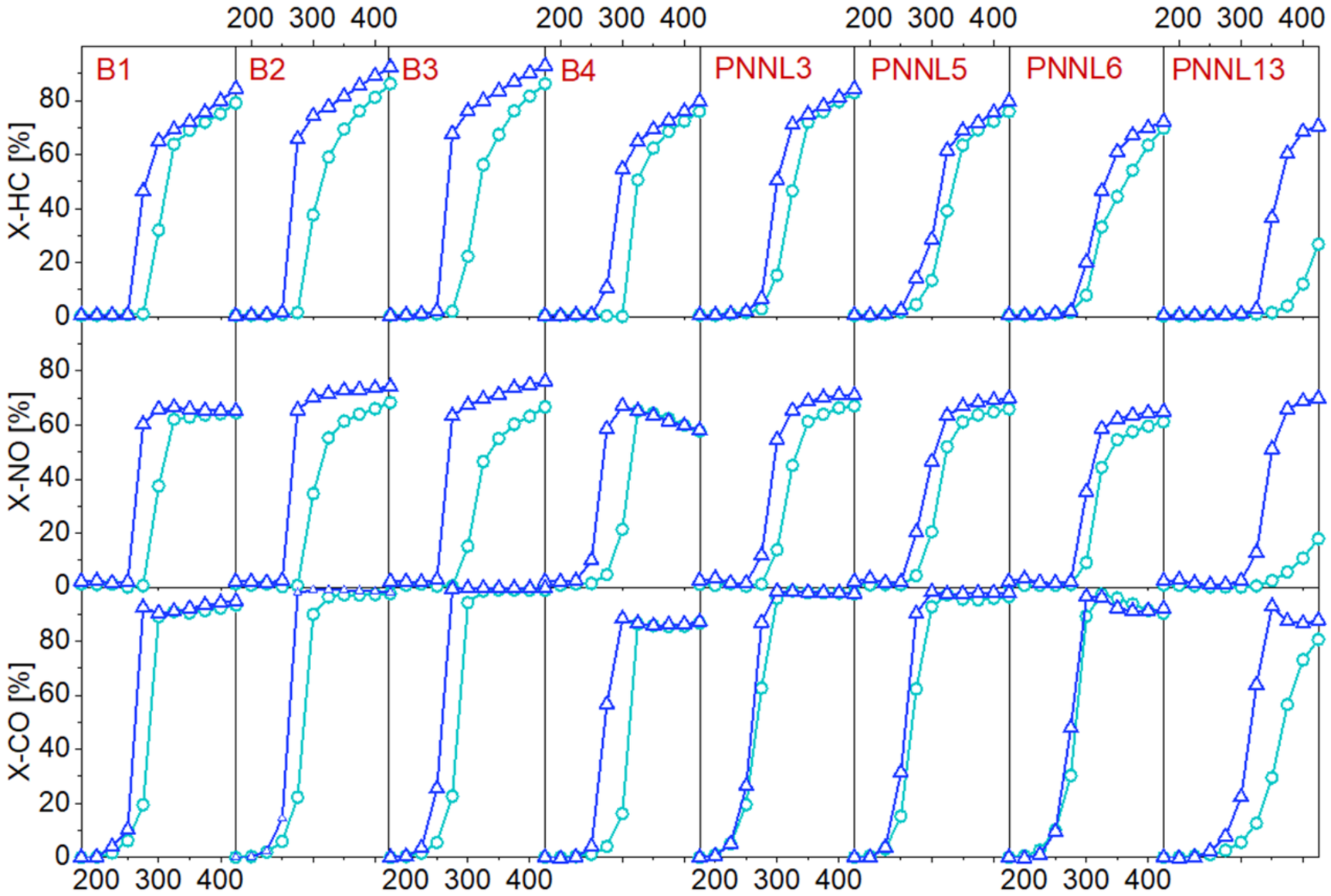
Summary

- Identified the potential challenge with atom trapping to selectively deposit Rh on the ceria domain of the commercially available supports (mixed ceria-alumina) provided by BASF, which is critical to further improvement of PGM efficacy.
- Developed a strategy to selectively deposit Rh on a commercially available ceria followed by wet grinding mixing with commercially available alumina.
- Identified a lead catalyst formulation based on commercially available supports, which gives similar performance with baseline catalysts but with 5x less Rh content.
- Catalyst synthesis was replicated at 100 gram scale for the core substrate washcoating.

Backup Slides

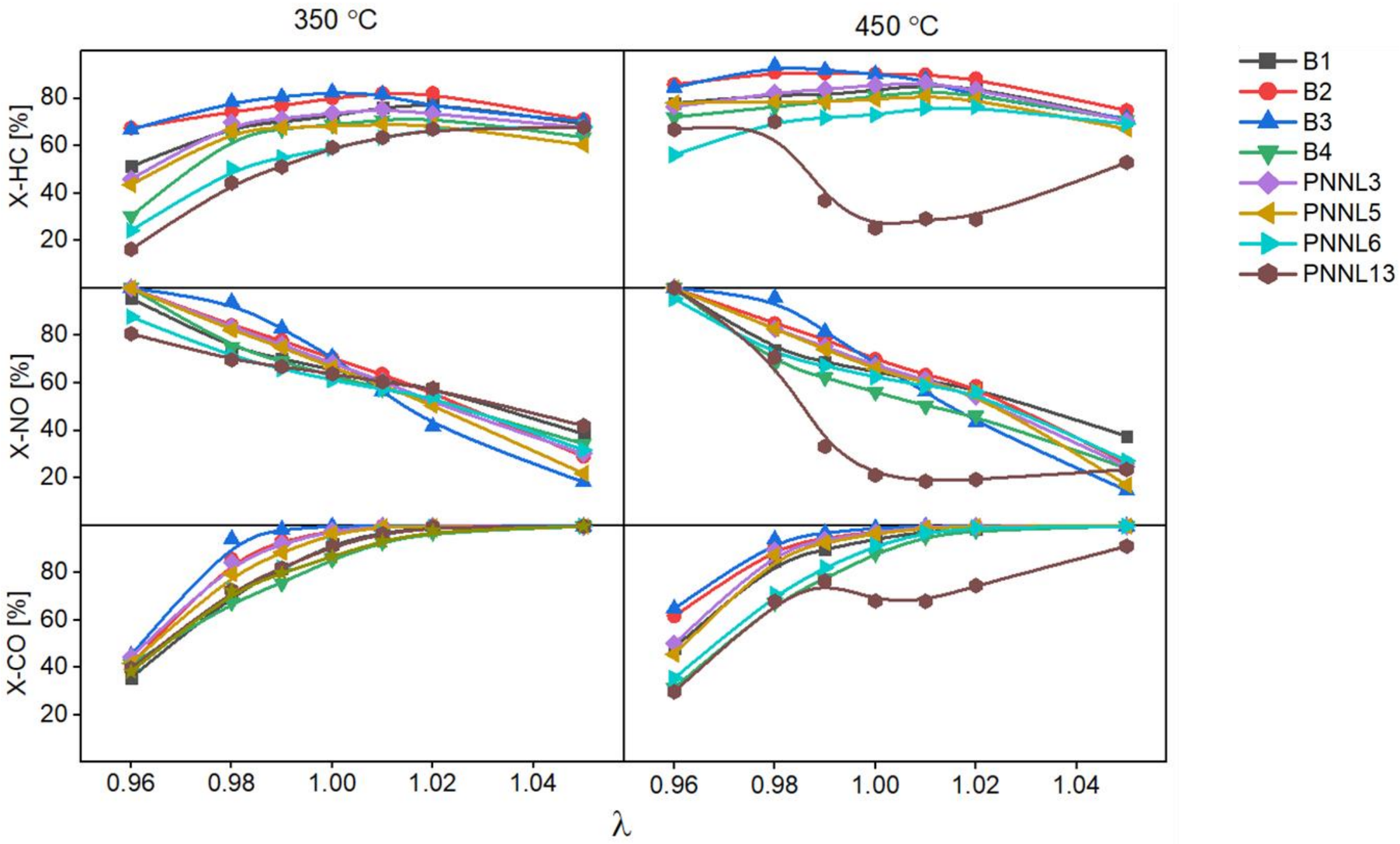
Technical Accomplishments and Progress

Comparison of baseline and SACs: light-off for HC, NO, and CO conversion before and after λ sweep



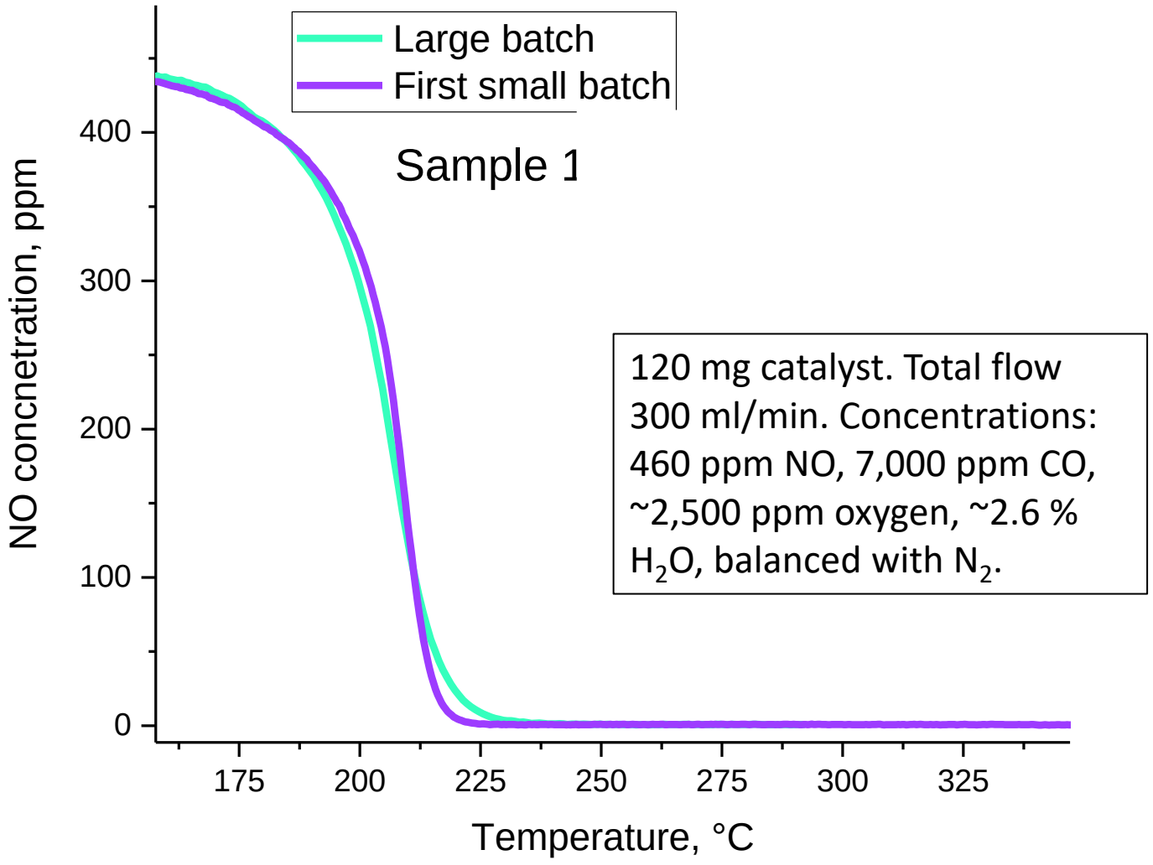
Technical Accomplishments and Progress

Comparison of baseline and SAC catalysts: HC, NO, and CO conversion as a function of λ sweep



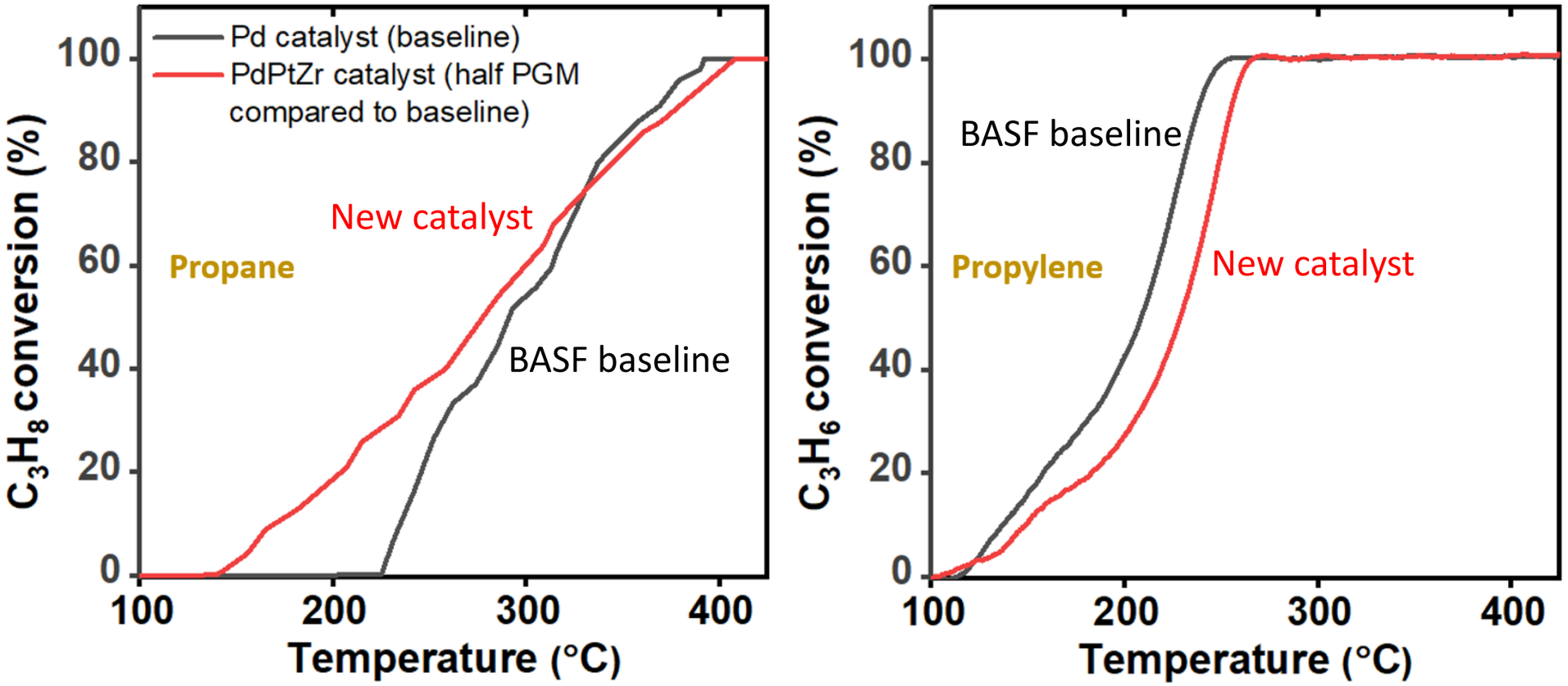
Identical Performance Was Achieved at >10 gram Scale

0.1Rh@ceria-alumina prepared by atom trapping: comparison between large (>10 gram) and small batch (<1 gram)



Similar Performance Was Also Achieved for HC Oxidation with 2x Less PGM

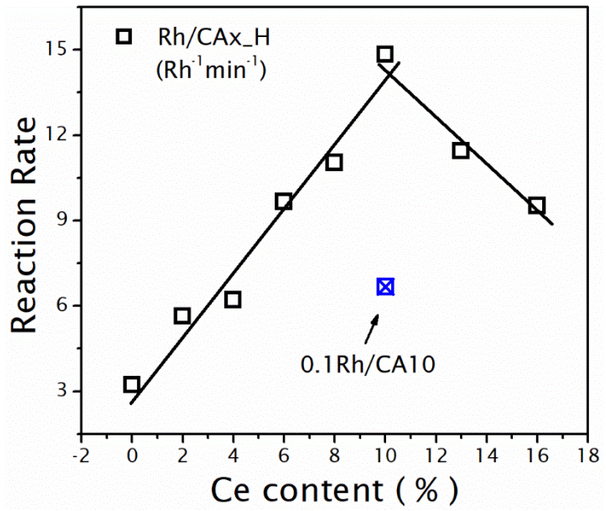
Light-off curves for propane and propylene oxidation on Pd catalyst (BASF 3wt% Pd/CA50, baseline) and PdPtZr catalyst with a nominal 1.5wt% Pd+Pt loading (1.5wt% Pd/CA50 + 1.5wt%Pt/2wt%Zr@CA50)

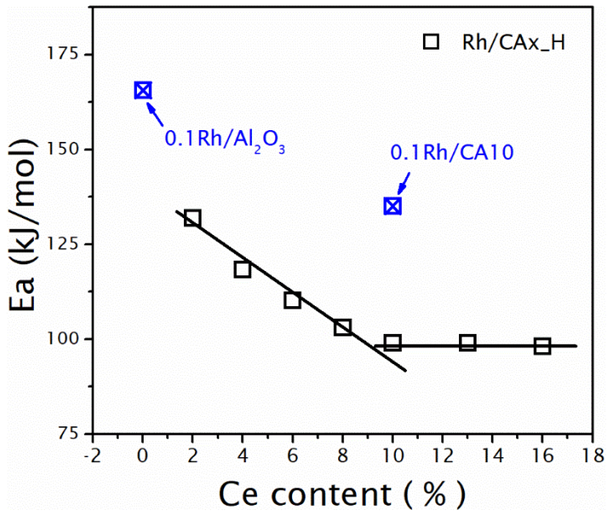


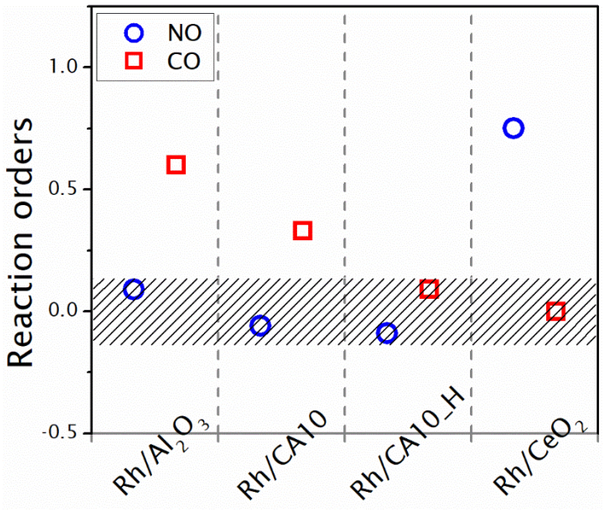
Total gas flow rate: 300 mL min^{-1}, 0.075 % NO, 0.67 % CO, 0.05 % C_3H_8, 0.05 % C_3H_6, and 0.64 % O_2 diluted in N_2

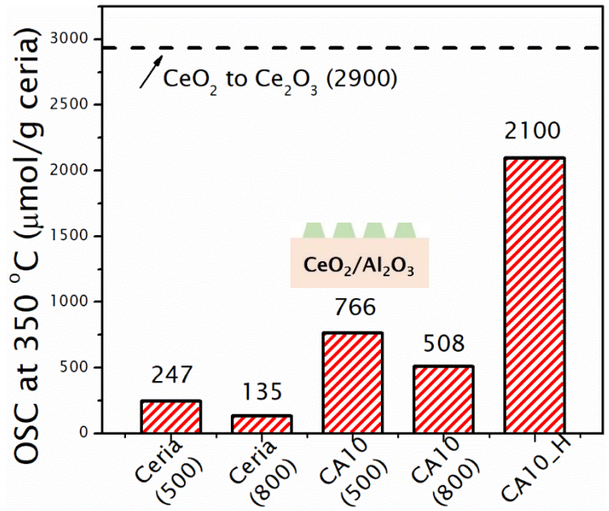
- Similar propane and propylene oxidation activity was achieved with 2x less total PGM (4x less Pd, replacing 50% Pt) by atom trapping compared with the baseline BASF 3wt%Pd/CA50 catalyst.

The content and state of ceria affect the performance

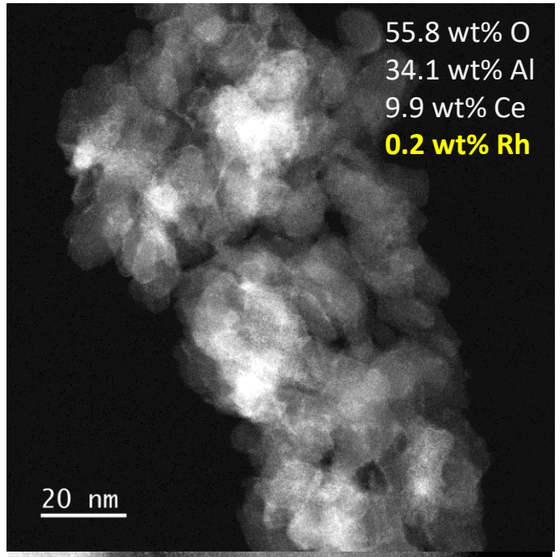


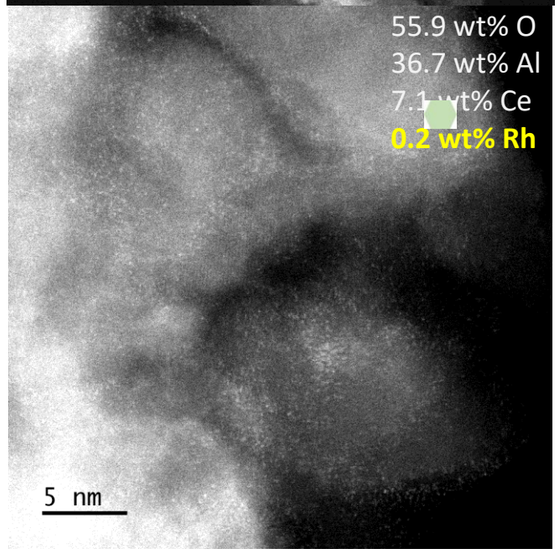






AC-STEM images of 0.1Rh@CA16_H_2, showing atomically dispersed Ce and Rh on alumina





- $Rh/Ce/Al_2O_3$ exhibits high TOF, low Ea, enhanced CO activation, high OSC